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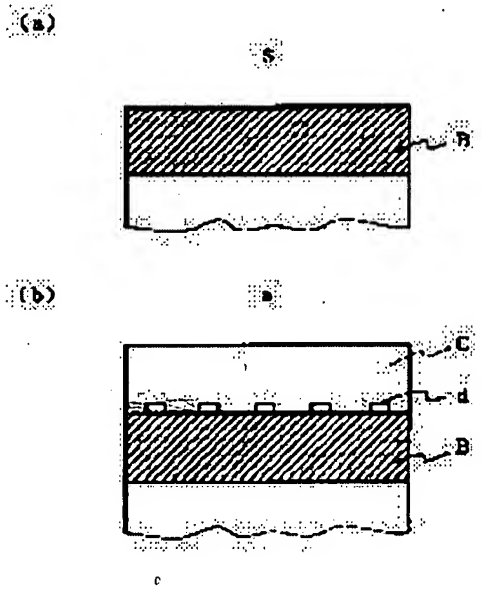
(54) FABRICATION OF GAN QUANTUM DOT STRUCTURE AND USE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for fabricating a new GaN quantum dot structure having a process simplified as compared with a conventional method and applicable to fabrication of semiconductor light emitting element.

SOLUTION: Surface state of the upper surface (base surface) of a base layer B composed of a GaN material is varied by an antisurfactant S and a GaN material having composition of three components and specific lattice matching performance is supplied to the base surface as a material gas (a) by vapor phase growth. Consequently, quantum dots (d) of a GaN material having compositional ratio different from that of the supplied GaN material are distributed on the base surface, and a cap layer C of a GaN material having compositional ratio identical to that of the supplied GaN based material is grown on the base surface while embedding the quantum dots (d) thus attaining a GaN quantum dot structure.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach and application of the quantum dot structure which consists of a GaN system ingredient.
[0002]
[Description of the Prior Art] Research is actively done on light emitting diode (LED) of quantity brightness being realized in recent years, and, as for a GaN system light emitting device, the report of the room temperature continuous oscillation of semiconductor laser is also heard.
[0003] Some which used the quantum well layer of InGaN for the luminous layer (barrier layer) are one of those from which luminescence of wavelength with short green - blue is obtained, and high luminous efficiency is moreover acquired also in a GaN system light emitting device. When forming a quantum well layer using InGaN, it does not become a uniform presentation ratio over the layer whole from the thermodynamic instability, but the part from which In presentation ratio differed locally in the layer occurs. This part has a property similar to a quantum dot. In the light emitting device using the quantum well layer of InGaN as a luminous layer, this quantum dot-part shows the operation which shuts up an exciton not only about the thickness direction of a layer but about a three-dimension-direction, and is said for the recombination radiation of a carrier to occur in this part, and this is set to one of the factors in which an InGaN quantum well layer may emit light with high luminous efficiency.
[0004] The quantum dot-part in an InGaN quantum well layer exists in an InGaN layer with the property of the InGaN itself. On the other hand, formation of the quantum dot using the grid mismatching of a dot ingredient and a substrate ingredient is known for the ingredient of a GaAs system. It became clear to these that the letter of a projection may be made to carry out crystal growth on this base side by making a GaN system semi-conductor with good this and grid adjustment into a quantum dot in recent years by performing special surface preparation to the front face (base side), and using specific vapor growth for it by using as a base layer the crystal layer which consists of a GaN system ingredient, (Appl.Phys.Lett.69 (1996) 4096). The mechanism of formation of this GaN system quantum dot completely differs from formation of said InGaN and the quantum dot in a GaAs system.
[0005]
[Problem(s) to be Solved by the Invention] Of the crystal growth which makes the remaining fields on a base side a start side, the above-mentioned GaN system quantum dot is formed until the layer (cap layer) which consists of another GaN system ingredient embeds this quantum dot, and it is made GaN system quantum dot structure. Therefore, in formation of such GaN system quantum dot structure, after performing surface treatment of a base side, first, in order to form a quantum dot, the ingredient only for quantum dots was supplied, next the ingredient was switched, and two steps of supplies of supplying the ingredient only for cap layers were performed.
[0006] The purpose of this invention is offering the manufacture approach of the new GaN system quantum dot structure the process's having been simplified more, compared with the manufacture approach of the above conventional GaN system quantum dot structures, and applying this to the

manufacture approach of a semi-conductor light emitting device further.
[0007]
[Means for Solving the Problem] The manufacture approach of the GaN system quantum dot structure by this invention has the following descriptions.
(1) Use as a base layer the crystal layer which consists of a GaN system ingredient, and make the top face of this base layer into a base side. The GaN system ingredient (A) which the surface state of this base side is changed by the anti surfactant, and has a 3 yuan or more presentation, and has the grid adjustment of following (i) by supplying a base side in vapor growth The quantum dot which consists of a GaN system ingredient of a different presentation ratio from the supplied GaN system ingredient (A), and is distributed on a base side, The manufacture approach of the GaN system quantum dot structure characterized by having the process which forms the crystal layer which consists of a GaN system ingredient of the same presentation ratio as the supplied GaN system ingredient (A), embeds said quantum dot, and grows on a base side.
[0008] The grid adjustment indicated below to be the grid adjustment of (i) as used in the field of the above and the following explanation is said.
(i) Grid adjustment over the GaN system ingredient of the base layer which can carry out crystal growth to the shape of film on this base side when carrying out crystal growth of the GaN system ingredient (A) directly on this base side, without performing surface preparation to which the surface state of a base side is changed.
[0009] (2) The crystal layer which embeds the above-mentioned quantum dot and grows on a base side In the mode of the repeat newly used as a base layer, formation with a quantum dot and the crystal layer which embeds this is repeated. it -- the beginning -- the base -- a field -- a top -- a quantum -- a dot -- this -- embedding -- a crystal -- a layer -- a group -- one -- a step -- ** -- carrying out -- this -- two -- a step -- more than -- a laminating -- carrying out -- multiplex -- a quantum -- a dot -- structure -- ** -- carrying out -- a thing -- it is -- the above -- (-- one --) -- a publication -- GaN -- a system -- a quantum -- a dot -- structure -- manufacture -- an approach .
[0010] (3) The manufacture approach of GaN system quantum dot structure the above (1) which is what chooses the ingredient of a base layer, and the GaN system ingredient (A) to supply so that it may become smaller than each band gap of the ingredient of a crystal layer with which the band gap of the ingredient of a quantum dot embeds the ingredient and this quantum dot of the base layer used as the base side of this quantum dot formation, or given in (2).
[0011] (4) The manufacture approach of the GaN system quantum dot structure the above-mentioned (1) publication which is what forms the quantum dot which consists of an ingredient of a presentation ratio with which aluminum component decreased rather than the AlGaN by setting to AlGaN the ingredient and the GaN system ingredient (A) to supply of a base layer.
[0012] Moreover, the application of the manufacture approach of the GaN system quantum dot structure by this invention is the manufacture approach of the GaN system semi-conductor light emitting device characterized by forming the GaN system quantum dot structure acquired by the manufacture approach of a publication by either of above-mentioned (1) - (4) as a part concerning luminescence.
[0013] On these specifications, hereafter the GaN system ingredient used for a base layer "A base ingredient", The crystal layer which embeds a quantum dot and grows on a base side "A cap layer", Each name is prepared, and the GaN system ingredient of a quantum dot with which a presentation changes and is formed of supply of a "cap ingredient" and a cap ingredient in the GaN system ingredient (A) supplied to a base side that a quantum dot and a cap layer should be formed is used together, and is explained to be a "dot ingredient." Moreover, GaN system quantum dot structure (only henceforth "quantum dot structure") means the structure where the quantum dot which consists of a GaN system ingredient was included with the GaN system ingredient of a presentation ratio with which the dot ingredients differ. Especially, the structure included with the larger ingredient of a band gap has a useful quantum dot to a light emitting device.
[0014]
[Function] When the GaN system ingredient was supplied on the base side where surface preparation

was made by the anti surfactant, the quantum dot was formed, but this invention person etc. got changing the mode of growth, and a presentation as new knowledge bordering on the fixed phase of quantum dot growth, when the GaN system ingredient to supply was a 3 yuan or more presentation. this invention person etc. made it possible to grow up a quantum dot by different presentation from this cap ingredient, to grow up the cap layer of the presentation which carried out this object of its call Fig. by fluctuation of oneself of that presentation ratio, and to acquire quantum dot structure within the limits of the element contained in that cap ingredient, first, by using this knowledge positively and continuing supplying only a cap ingredient.

[0015] Here, as a GaN system ingredient carries out crystal growth, it is supplying material gas on a base side under the conditions of vapor growth in the ratio of an element with which this GaN system ingredient's is formed as supplying material gas in vapor growth. For example, in order to carry out crystal growth of the AlGaN as a GaN system ingredient, it is supplying ammonia as trimethylgallium (TMG) and an N raw material as trimethylaluminum (TMA) and a Ga raw material as an aluminum raw material etc.

[0016] Although feed, growth conditions, etc. were switched to two steps by the conventional manufacture approach, having made growth of a quantum dot into the 1st step, and having used growth of a cap layer as the 2nd step By the manufacture approach of this invention, no modification and change of feed or growth conditions are performed, but supplying the raw material for growing up a cap layer from the beginning is only continued, the quantum dot of a different presentation ratio from it is grown up, and the cap layer of a presentation ratio as supplied further is grown up.

[0017] However, a base ingredient and a cap ingredient have the relation of the above (i). That is, when growing up a cap ingredient on a base side on a crystal growth method and growth conditions as usual, without changing the surface state of a base side in any way, a cap ingredient is an ingredient which grows considering a base side top as a whole surface wrap crystal layer as film as known conventionally. that is, both a base ingredient and a cap ingredient are GaN system ingredients, and I hear that it is alike to that extent and lattice matching is carried out at least, and it is.

[0018] When the raw material with which a base ingredient and a cap ingredient constitute a cap ingredient in the condition of having the relation of the above lattice matching is supplied, in order for the mode of a crystal which grows on a base side to serve as a quantum dot, the anti surfactant (matter to which the surface state of the GaN system crystal layer front face which is a base side is changed) is made to act on a base side. Although not solved in detail about change of the surface state of the GaN system crystal layer front face by operation of the anti surfactant, it is thought that it is change to which surface free energy becomes small. By changing the surface state of a base side in this way, out of the raw material which constitutes a cap ingredient, crystal growth is carried out as a quantum dot on a base side, the mode of a presentation ratio and growth is changed in the phase which grew to fixed magnitude, and the GaN system ingredient of a different presentation ratio from a cap ingredient changes to the cap layer which embeds a quantum dot.

[0019]

[Embodiment of the Invention] Drawing 1 is the sectional view showing signs that GaN system quantum dot structure is formed by the manufacture approach of this invention. The crystal layer which consists of a GaN system ingredient is used as the base layer B, and the top face of this base layer is made into a base side. The base layer B is arranged in the tub of vapor growth equipment, and the GaN system ingredient serves as an environment in which crystal growth is possible on the base side. As first shown in drawing 1 (a), supply the anti surfactant S in a tub, a base side is made to contact, and that surface state is changed from this condition. Next, the gas a containing the raw material corresponding to the GaN system ingredient (cap ingredient) which has a 3 yuan or more presentation is supplied to a base side. A cap ingredient shall have the grid adjustment of the above (i) to a base ingredient.

[0020] Only by continuing supply of this material gas a, as shown in drawing 1 (b), the quantum dot d distributed on a base side grows, further, this quantum dot d is embedded and the cap layer C grows. At this time, the presentation ratio of the matter which constitutes the quantum dot d becomes a different thing from the presentation ratio of a crystal which should grow essentially with the supplied raw

material, and the presentation ratio of the matter which constitutes the cap layer C becomes the crystal itself which should grow essentially with the supplied raw material.
[0021] The GaN system ingredient as used in the field of this invention, it is expressed with Formula InX GaY AlZ N (0<=X<=1, 0<=Y<=1, 0<=Z<=1, X+Y+Z=1). It is an III group nitride semi-conductor.
[0022] Although the ingredient of a base layer should just be a nitride semi-conductor expressed with said formula, if quantum dot structure is used as a part for the light-emitting part of a light emitting device, the large thing of a band gap of the ingredient of a base layer will be more desirable than the ingredient of a quantum dot.
[0023] Surely let the cap ingredient supplied on a base side be the nitride semi-conductor of 3 yuan or 4 yuan among the nitride semi-conductors expressed with said formula. In having supplied the 2 yuan ingredient as a cap ingredient, it is because the quantum dot from which there is no fluctuation of an effective presentation ratio substantially, and a cap ingredient and a presentation ratio differ is not formed.
[0024] The cap ingredient of what kind of presentation is supplied on a base side, it is not limited of what kind of presentation a quantum dot is grown up from there, but it should just choose the GaN system ingredient of 3 yuan or more as a cap ingredient according to the purpose. AlGaN is mentioned as an example of an ingredient useful as a light-emitting part of a light emitting device. By supplying AlGaN as a cap ingredient, AlGaN as the quantum dot (namely, quantum dot with a band gap smaller than a cap layer) which consists of an ingredient of a presentation ratio with which aluminum component decreased was grown up and being supplied rather than the AlGaN can be used as a cap layer.
[0025] In order to form a quantum dot in a base side, the matter (anti surfactant) from which the surface state is changed to a base side is made to act, as explanation of the above-mentioned operation described. What is necessary is just to contact a base side and the anti surfactant, in order to make the anti surfactant act on a base side. although the approach of contact is not limited -- MOCVD -- what is necessary is just to supply the gas anti surfactant in this equipment by law, after an AlGaN crystal layer grows within an MOCVD system if it is the case where an AlGaN crystal layer top face is made into a base side Then, a cap ingredient is supplied and quantum dot structure is formed.
[0026] If a tetraethyl silane is made into the anti surfactant in order to supply the anti surfactant as a gas for example, it will be H2 to the solution. By carrying out bubbling of the gas, it is H2. The approach of supplying gas as carrier gas is mentioned.
[0027] The matter used as anti surfactant can choose a suitable thing, and is not limited by combination with the cap ingredient supplied with a base ingredient that what is necessary is just the matter from which the surface state of a base side is changed to extent the GaN system ingredient which has the grid adjustment of the above (i) grows up to be in the shape of a dot. For example, by using an AlGaN crystal layer as a base layer, when supplying the raw material of AlGaN and making a quantum dot form on this base side, a tetraethyl silane is mentioned as anti surfactant. In addition, SiH4, Si two H6 or these mixed gas, Cp2 Mg (bis(cyclopentadienyl) magnesium), etc. are mentioned.
[0028] The crystal growth approach including the feeding method when growing up a quantum dot and a cap layer is mentioned as an approach that MOCVD, MBE, etc. are especially desirable that what is necessary is just to follow vapor growth.
[0029] The degree of distribution of the magnitude of each quantum dot, a configuration, and a quantum dot is controllable by changing the presentation of the amount of supply of the anti surfactant, the growth temperature of a quantum dot, and a base ingredient as a parameter.
[0030] Although the above is the approach of manufacturing one quantum dot structure, multiplex quantum dot structure can be easily formed by repeating this. That is, as five steps of examples are given and shown in drawing 2 , the group of this quantum dot and a cap layer is counted as one step in the condition of having formed the quantum dot d1 and the cap layer B1, and having become quantum dot structure by supply of the cap ingredient to the top face of the base layer B first. By making the top face of the cap layer B1 into a base side, a cap ingredient is supplied again, on the first base layer B, as - (d1, B1) (d5, B5), the laminating of the group of a quantum dot and a cap layer is carried out to five steps,

and it is newly made into multiplex quantum dot structure in the mode of the repeat of growing up the group of the quantum dot d2 and cap layer B-2.

[0031] The band gap of the quantum dot formed in each stage of multiplex quantum dot structure should just choose the cap ingredient to supply so that it may become smaller than the band gap of the ingredient of the base layer. In multiplex quantum dot structure, as long as the relation of the band gap of the quantum dot and the ingredient of a perimeter of each stage satisfies this condition, a mutually different band gap is sufficient as the cap ingredients of each stage.

[0032] The quantum dot structure acquired by this invention can be preferably used as a part concerning the luminescence in a semi-conductor light emitting device, as shown in drawing 3 . When the luminescence is a phenomenon which an electron and a hole recombine and emits light in a quantum dot by impregnation of an electron or a hole, it is necessary from the band gap of a base ingredient and a cap ingredient to make small the band gap of the ingredient which constitutes a quantum dot. As a desirable cap ingredient which fills such relation, as described above, AlGaN is mentioned. Moreover, in order to acquire the difference of a big band gap with a quantum dot in that case, also as for a base ingredient, being referred to as AlGaN is desirable.

[0033] The example of manufacture of the GaN system light emitting device using the manufacture approach of the quantum dot structure by this invention is shown in drawing 3 . This drawing shows LED of the easy structure for explanation as an example. As shown in this drawing, the layered product S including the quantum dot structure 3 which is made to carry out sequential growth of the crystal layer which consists of a GaN system ingredient, puts, and is formed of the above-mentioned explanation on the crystal substrate 1 is formed, and the electrode 6 by the side of p mold and the electrode 7 by the side of n mold are prepared and constituted in this. p mold cladding layer and the layer 5 in which a layer 2 makes n mold contact layer, and a layer 4 makes the base layer B (n mold cladding layer) and a pair are p mold contact layer, and all consist of a GaN system ingredient.

[0034] The vertical physical relationship of the conduction type (p mold, n mold) in the example of drawing 3 is the general thing which uses a crystal substrate side as n mold, and uses an upper layer side as p mold from the reasons of processing for forming a conduction type. Moreover, in the example of this drawing, the insulator (sapphire crystal substrate) is used for the crystal substrate, the top face of a layer 2 is exposed, and it has become arrangement of the electrode of forming an electrode 7 in the field. However, a mode with the reverse upper and lower sides of a p/n mold, electrode disposition in case a crystal substrate has conductivity, etc. may be chosen freely.

[0035] What is necessary is for the conduction type of the base layer B in the quantum dot structure 3 of drawing 3 and the cap layer C to be the same, or to differ mutually, and just to choose them by how it uses as a part for the light-emitting part in a light emitting device. In the example of drawing 3 , the quantum dot structure 3 consists of a base layer B (it functions as an n mold cladding layer) of the 1st conduction type (drawing n mold), and many quantum dots d (undoping) and the cap layer C (undoping), and p mold cladding layer 4 is further formed on it. Moreover, it is good also as structure which considered the base layer B of drawing 3 as undoping, and prepared the cladding layer of n mold in the bottom separately.

[0036] As described above, both let magnitude of each band gap of a base ingredient and a cap ingredient be a larger thing than the magnitude of the band gap of a dot ingredient in a light emitting device. This is for pouring an electron and a hole into the quantum dot which is a light-emitting part efficiently.

[0037] The sapphire and Xtal which are used widely in case a GaN system crystal is grown up from the former, SiC, etc. are mentioned by the crystal substrate just possible [growth of a GaN system crystal]. Especially, C side, the Ath page, 6 H-SiC substrate, especially C side silicon on sapphire of sapphire are desirable. Moreover, buffer layers, such as ZnO for easing the difference in a lattice constant with a GaN system crystal or a coefficient of thermal expansion, MgO, and AlN, may be prepared in the front face of these ingredients, and it may have the thin film of a GaN system crystal on a surface further. In the example of drawing 3 , that by which buffer layer 1b for improving grid adjustment was formed on sapphire crystal substrate 1a used as a foundation is used as a crystal substrate 1.

[0038]
[Example] In this example, LED of the structure shown in drawing 3 was actually manufactured, using the manufacture approach of the quantum dot structure by this invention. In this example, it is the example in which the quantum dot structure 3 which consists of an AlGaN base layer B, and the quantum dot d and the AlGaN cap layer C was formed into the light emitting device, by setting the base ingredient in a part for the quantum dot structured division to AlGaN, and carrying out feeding of the AlGaN as a cap ingredient. The quantum dot structure 3 set the base layer (n mold cladding layer) B to aluminum0.15Ga0.85N, and set the cap layer C to aluminum0.1 Ga0.9 N of undoping. When the presentation of the formed quantum dot was investigated at this time, aluminum was below limit of detection and was the presentation which can be substantially treated as GaN. Moreover, the ingredient of p mold cladding layer 4 was set to aluminum0.15Ga0.85N.
[0039] [Formation of the crystal substrate 1] As basic crystal substrate 1a, the sapphire C side substrate was used most. This silicon-on-sapphire 1a has been first arranged in an MOCVD system, the temperature up was carried out to 1200 degrees C under the hydrogen ambient atmosphere, and thermal etching was performed. Temperature was lowered to 500 degrees C after that, ammonia is grown up as an aluminum raw material, 30nm sink and AlN low-temperature buffer layer 1b was grown up as TMA and an N raw material, and the crystal substrate 1 was obtained.
[0040] [Formation of n mold contact layer 2] The temperature up of the growth temperature is carried out to 1000 degrees C, as a Ga raw material, the silane was grown up as TMG and an N raw material, and a sink and 3 micrometers of n mold GaN contact layers 2 were grown up as ammonia and a dopant raw material.
[0041] [Formation of the quantum dot structure 3]
** Formation of the base layer B; growth temperature was made into 1100 degrees C, the silane was supplied as TMA, TMG, ammonia, and a dopant raw material, and 0.5 micrometers of base layers B which consist of n mold aluminum0.15Ga0.85N were grown up. The base layer B is a layer which achieves the function as an n mold cladding layer.
[0042] ** Surface preparation of a base side; make temperature into 1000 degrees C and it is H2. The tetraethyl silane was supplied by having used gas as the carrier, and the base side was made to contact for 10 seconds.
[0043] ** Formation of the quantum dot d and the cap layer C; when growth temperature was made into 1100 degrees C and TMA, TMG, and ammonia were supplied, on the base side, the quantum dot d grew first, and the AlGaN cap layer C grew so that this might be embedded further inside. As described above, the ingredient which constitutes a quantum dot was what can be substantially said to be GaN. The thickness of the cap layer C could be 20nm.
[0044] [Formation of p mold cladding layer 4] Growth temperature was made into 1100 degrees C, bis (cyclopentadienyl) magnesium (Cp2 Mg) was supplied as TMA, TMG, ammonia, and a dopant raw material, and 0.5 micrometers of cladding layers 4 which consist of p mold aluminum0.15Ga0.85N were grown up.
[0045] [Formation of p mold contact layer 5] Growth temperature was made into 1000 degrees C, Cp2 Mg was supplied as TMG, ammonia, and a dopant raw material, and 1 micrometer of p mold GaN contact layers 5 was grown up.
[0046] [Formation of an electrode] etc. The sample was taken out from equipment and annealing treatment was performed for 20 minutes at nitrogen-gas-atmosphere mind and 800 degrees C. Finally, p mold electrode 6 was formed on p mold contact layer 5, and etching removal of a part of p type layer and quantum dot structure was carried out from the top face of a layered product by dry etching, and the top face of n mold contact layer 2 was exposed, n mold electrode 7 was formed, and it was referred to as LED.
[0047] When this LED was mounted on the To-18 stem base and luminous intensity in 20mA was measured, it is 50mcd and it turned out that it is the light emitting device which has the outstanding luminescence property.
[0048]

[Effect of the Invention] As mentioned above, by the manufacture approach of this invention, the process of feeding can be simplified more, GaN system quantum dot structure can be manufactured now, and it can take in now preferably as the manufacture approach for a light-emitting part also to manufacture of a GaN system semi-conductor light emitting device.

[Translation done.]